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Preparation and Characterization of Phosphate Film for Magnesium Alloy AZ31

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Abstract

An anticorrosion phosphate film with free of chromate, fluorides and nitrite, was successfully prepared on the surface of the magnesium alloy AZ31 via chemical deposition method. The effects of film-forming temperature and free acid on the corrosion resistance of the film were investigated through SEM. The analysis results indicate that the compactness of the film increased with the increase of film-forming temperature, but more residues is brought. While increasing FA in the proper range can decrease the residues. The EDS characterizations of the film confirm that the phosphate film contains only three elements of Mn, P and O. The analysis of the polarization curves further prove that the film has great inhibitive action on anodic dissolution and cathodic hydrogen evolution, and the corrosion resistance is improved with the increase of temperature.

Keywords: Magnesium alloy; Phosphate film; Corrosion resistance; Chrome-free;

1. Introduction

Magnesium alloys exhibit some attractive properties of low density, high specific strength, associated with good damping and electromagnetic shielding ability, which make them ideal candidates for light-weight engineering applications, for instance, in communication, computer, automobile and aerospace [1-2]. However, the poor corrosion resistance of magnesium alloys restricts their use on a larger scale, especially suffers dissolved contaminants from solid, liquid and gas in a moist exposed atmosphere to

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form electrolyte [3]. Therefore, it is vital to improve the corrosion resistance of magnesium alloy. Among various corrosion protection methods, chemical conversion film is the most common method for lower cost and more convenient use. However, because of the high toxicity of the hexavalent chromium ions, the most popular and effective chromate bath have been progressively restricted [4]. Recently, several studies of environmentally friendly chemical conversion film treatment have been focused on the magnesium alloys, such as the phytic acid conversion film [5], oxalate films [6], cerium conversion films [7,8], stannate conversion films [9], silane films [8] and phosphate films [10]. In these methods, phosphate films are widely applied because of good corrosion resistance and contact between paint and metal surface [11]. However, the conventional phosphate solutions [10, 11] contain many hazardous substances such as fluorides, nitrites and heavy metal elements, which are not environmentally friendly.

In the present work, an environmentally friendly phosphate solution with free of chromate, fluorides and nitrite has been prepared, and the better corrosion resistance phosphate film was deposited on the surface of the magnesium alloy AZ31. The effects of film-forming temperature and free acid on corrosion resistance of the film were discussed. The surface morphologies and composites of the film were characterized by means of SEM and EDS. The corrosion resistance of the film was also evaluated through polarization curves.

2. Experimental set-up

The substrate material was AZ31 magnesium alloy (compositions / wt%: 2.96% Al, 0.89% Zn, 0.37% Mn, 0.0134% Si, 0.001% Cu, 0.002% Ni, 0.0027% Fe, with the remainder being Mg, thickness of 2.0 mm, supplied by a company). Before deposition treatment, the pretreatments of the substrate were carried out and listed as follows: abrading (water-proof abrasive papers from 300-800 grades) → distilled water bath → alkali wash (60%NaOH) → distilled water bath → acid activation (75%H_3P0_4) →distilled water bath → surface conditioning → phosphating → drying (120℃,20min).

All chemicals were of reagent grade and used without further purification. The compositions of the phosphate solution were chosen according to the reference [12]. The pH of the solution was adjusted to 3.0-6.0 by H_3PO_4 and NaOH. In order to prepare the corrosion resistance conversion film, the AZ31 magnesium alloy samples were treated in the temperature range of 75-95 ℃ for 25 min in the phosphate solution.

The surface morphologies and the compositions of the obtained films were studied using scanning electron microscopy (SEM, VEGA 3 SBU, Europe) with Energy Dispersive Spectrometer (EDS, England Oxford).

All the electrochemical experiments were carried out in 3.5% NaCl solution at room temperature using the electrochemical system (PARSTAT 2273, America). The test instrument was composed of three-electrode system. A saturated calomel electrode (SCE) was used as a reference electrode. The platinum sheet with a surface area of 5 cm^2 was used as an auxiliary electrode. The sample with a surface area of about 1 cm^2 was the working electrode. The potentiodynamic electrochemical tests were carried out with a scan rate of 1 mV/s.

3. Results and discussion

3.1. Surface morphology

The free acid (FA) and the film-forming temperature are two important parameters for the phosphating. They have great effects on the film-forming rate through controlling the dissociation degree of the soluble phosphate [10]. Fig. 1 represents surface morphologies of the phosphate film at different FA and film-forming temperatures. It can be observed from Fig.1 (a), (b) and (c) that the particles on the substrate surface increase gradually in number with the increase of FA from 3.0 to 5.0 at 75 ℃, but the substrate is still visible. The results indicate that the dense film can not be obtained at a relative lower temperature. When the film-forming temperature is 95℃, the relative denser film is observed from Fig.1 (d), (e) and (f). However, the surface of the films from Fig.1 (d) and (e) are unclear compared with that of the Fig. 1(f). This is because the dissociation degree of the soluble phosphate will increase with the temperature increasing, which can lead to dramatic increasing of the concentration of the film-forming ions and plenty of residues phosphide. The phosphate residues deposit to the surface of the phosphate film, and have great effects on the quality of the film. The FA is effective to control the dissociation degree of the soluble phosphate and the concentration of the ions. With the FA increasing, the surface can become clearer, denser and phosphate residues will almost disappear (Fig.1 e). In summary, the results prove that raising film-forming temperature will make the film denser but bring plenty of residues. While increasing FA in the proper range can decrease residues, which is very favorable to reduce cost and prolong the use life of the phosphate solution.

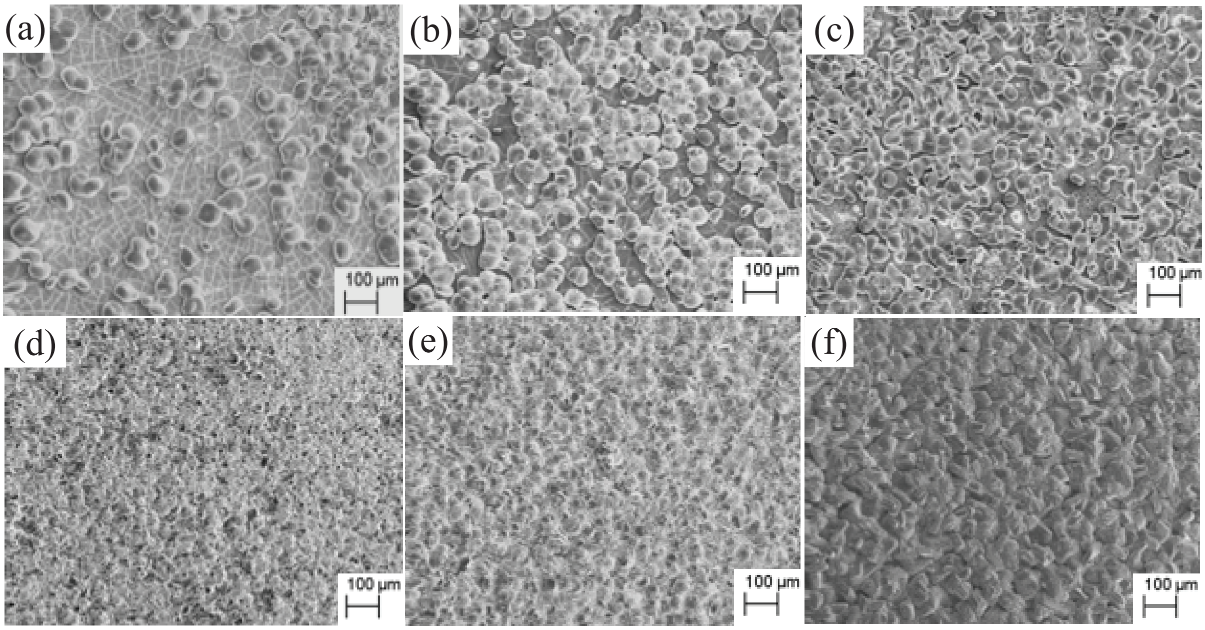

Fig. 1 Surface morphologies of phosphate films at different FA and film-forming temperature

(a) FA 3.0,75℃ (b) FA 4.0,75℃ (c) FA 5.0,75℃ (d) FA 3.0,95℃ (e) FA 4.0,95℃ (f) FA 5.0,95℃

3.2. Compositions

To prove the phosphate film is chromium-free, fluorine-free and no nitrite, the EDS was used for analyzing the composition of the phosphate film. Fig. 2 shows surface morphology and elements distribution of the film after 1 min phosphating. Nearly circle particles and substrate coated certain substance can be observed from the SEM photo, so two positions at different area were chosen to analyze the compositions. Some peaks originate from Mg, Mn, P, O and Al can be observed from the position of the spectrum 1, but only peaks of Mn, P and O are obtained from the position of the spectrum 2. Moreover, the peaks assigned to Mg and Al are ascribed to the AZ31 magnesium alloy substrate. Therefore, the phosphate film is mainly composed of three elements of Mn, P and O. Compared the surface morphology photo of Fig. 2 and that of Fig. 1(f), we can acquire that the film is also formed by the deposition process of the insoluble phosphate [13], and the process may be divided into three parts, i.e. deposition- nucleation-growth, so nucleation agents have great effects on the forming of the phosphate film.

3.3. polarizations

Corrosion current density (I_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p) are often used to evaluate the corrosion protective property of coatings [7, 9]. Fig. 3 shows the potentiodynamic polarization curves tested in 3.5 wt% NaCl solutions for the blank magnesium alloy AZ31 and the phosphate samples at different film-forming temperatures. The corrosion parameters were calculated through self-bring soft and listed in the Table 1. The anode polarization curves appear good linearity in the range of Tafel extrapolation, so the corrosion rate can be estimated from the polarization curves [3, 14]. The E_{corr}, I_{corr} and R_p of the blank AZ31 are -1566 mV (vs. SCE), 5.02×10^{-4} A/cm^2 and 69 $\Omega\cdot$cm^2, respectively. Compared with the phosphating samples, the E_{corr} and R_p are lower and the I_{corr} is considerable higher, which imply that the phosphate film has much higher corrosion resistance than the bare substrate. When the film-forming temperature is 75 ℃, the E_{corr}, I_{corr} and R_p are -1543 mV (vs. SCE), 1.68×10^{-6} A/cm^2 and 24566 $\Omega\cdot$cm^2, respectively. However, when the film-forming temperature arrive to 95℃, the E_{corr} is shifted positively 70 mv (vs. SCE), the I_{corr} is decreased approximately by three magnitude orders and the R_p is increased by 1711 times compared with that of the bare substrate. The results indicate the corrosion resistance performance is enhanced gradually with the increasing of film-forming temperature. The phosphate film plays a key role in improving the corrosion resistance of the AZ31 magnesium alloys.

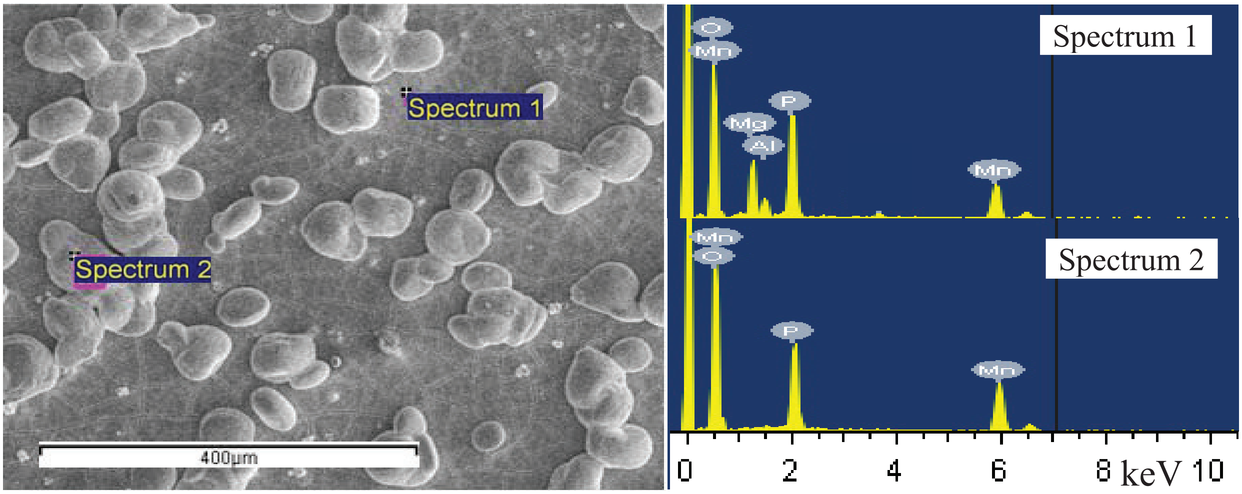

Fig. 2 Surface morphology and elements distribution of the film after 1 min phosphating

Table 1 Relevant electrochemical parameters of potentiodynamic polarization curves calculated from the Tafel plot

	E_{corr} (mV/SCE)	I_{corr} (A/cm^2)	R_p / (Ω·cm^2)
Blank AZ31	-1566	5.02×10^{-4}	69
75℃ phosphating	-1543	1.68×10^{-6}	24566
95℃ phosphating	-1496	1.36×10^{-7}	118110

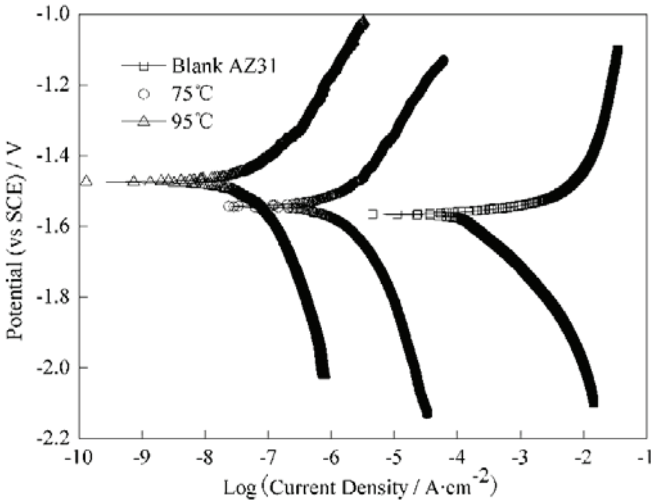

Fig. 3 Potentiodynamic polarization curves tested in 3.5 wt% NaCl solutions for the blank magnesium alloy AZ31 and the phosphate samples at different film-forming temperatures

4. Conclusions

An anticorrosive phosphate film with good compactness was successfully deposited on the magnesium alloy AZ31 by chemical deposition method, and the film is chromium-free, fluorine-free and no nitrite. In the preparation process, the film-temperature, FA and nucleation agent have great effects on the corrosion resistance. In addition, the insoluble phosphates improve greatly the corrosion resistance of magnesium alloy AZ31 through the inhibitive action on anodic dissolution and cathodic hydrogen evolution. Certainly, the anticorrosive property can also be further improved by understanding the anticorrosive mechanism, controlling the film density and decorating the surfaces with functional paints.

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